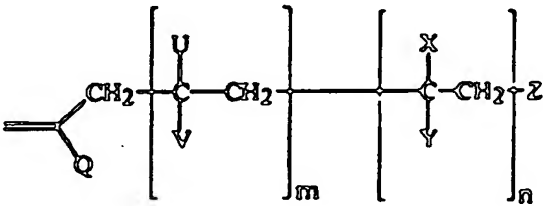




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> POLYMER SYNTHESIS <b>(57) Abstract</b> <p>Process for the synthesis of block polymers, homopolymers and copolymers of narrow polydispersity having formula (I) by contacting selected vinyl monomer(s), vinyl-terminated compound(s) and free radicals in which effective control of production of polymer is achieved by controlling the mole ratio of vinyl monomer(s), vinyl-terminated compound(s) and free radicals relative to one another, and polymers produced thereby.</p> <div style="text-align: center;">  <p>(I)</p> </div>		

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# TITLE POLYMER SYNTHESIS

## 1. Field of the Invention

5 This invention relates to a process for the synthesis of block copolymers and polymers of narrow polydispersity based on radical polymerization of monomers in the presence of unsaturated chain transfer agents.

## 2. Background

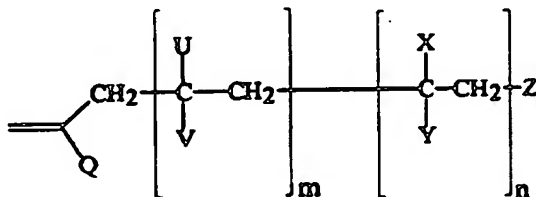
10 Block copolymers are useful as pigment dispersants, surfactants, compatibilizers for polymer blends, thermoplastic elastomers and in a variety of other applications. Polymers with narrow molecular weight dispersity can enhance melt viscosity behavior, solids-viscosity relationships of polymer solutions and sharper melt transitions than the same composition at a higher polydispersity.

15 Conventional commercial techniques for synthesizing narrow polydispersed polymers and block copolymers include free-radical polymerization. Radical polymerization may be accomplished: (1) through the use of pseudo or quasi-living polymerization. These techniques make use of low molecular weight transfer agents and/or chain terminators; (2) through the use of transformation chemistry; (3) through the use of multifunctional or polymeric initiators.

20 This invention provides a method of employing certain vinyl compounds in the synthesis of polymers with narrow molecular weight distribution and block copolymers by free radical polymerization. Block copolymerization by radical polymerization has been described in PCT Application No WO 93/22355. This PCT application describes the mechanism of block copolymer formation but does not define  
25 conditions necessary for the preparation of high purity block copolymers, nor formation of narrow polydispersity resins.

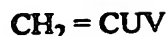
## SUMMARY OF THE INVENTION

30 This invention is directed to a process for the synthesis of polymers (block, homo- and copolymers) of the general formula:

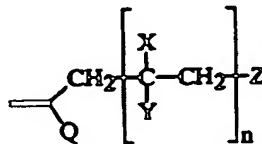


comprising contacting:

(i) a vinyl monomer of the formula



(ii) a vinyl-terminated compound of formula



2

5 and

(iii) free radicals, produced from a free radical source; and  
increasing the molar amount of polymers, 1, by one or both of:

(a) decreasing the molar amount of (iii) for any given conversion of (i);  
and

10 (b) decreasing the molar amount of (i) for any given conversion of (iii);

wherein:

Q is selected from the group H, R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN,  
CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;

U is selected from H and R;

15 V is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR  
and CONR<sub>2</sub>;

X is selected from H and R;

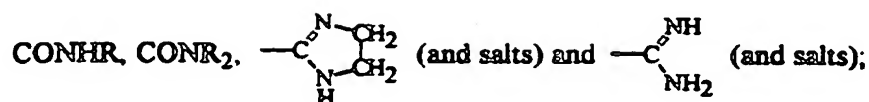
Y is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR  
and CONR<sub>2</sub>;

20 Z is selected from the group H, SR<sup>1</sup>, S(O)R, S(O)<sub>2</sub>R, R<sup>2</sup> and R<sup>3</sup>;

R is selected from the group substituted and unsubstituted alkyl, aryl, aralkyl,  
alkaryl and organosilyl groups wherein the substituent(s) are independently  
selected from the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

25 R<sup>1</sup> is selected from the group H, substituted and unsubstituted alkyl, aryl, aralkyl,  
alkaryl, organosilyl wherein the substituent(s) are independently selected from  
the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

30 R<sup>2</sup> is selected from the group free radical initiator-derived fragments of substituted  
and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl,  
alkoxyaryl, sulfate groups wherein the substituent(s) are independently selected  
from R, OR<sup>1</sup>, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H (and salts), CO<sub>2</sub>R, CN, CONH<sub>2</sub>.



R<sup>3</sup> is selected from the group radical chain transfer agent-derived fragments of substituted and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl, alkoxyaryl, and PR<sub>2</sub> groups wherein the substituent(s) are  
 5 independently selected from R, OR<sup>1</sup>, SR, NR<sub>2</sub>, NHR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR, and CONR<sub>2</sub>;

m and n are independently  $\geq 1$ ; and

when either or both of m and n are greater than 1, the repeat units are the same or different.

10 Each alkyl in the defined substituents is independently selected from branched, unbranched, and cyclical hydrocarbons having 1 to 20, preferably 1-12, and most preferably 1-8 carbon atoms; halo or halogen refers to bromo, iodo, chloro and fluoro, preferably chloro and fluoro, and organosilyl includes -SiR<sup>4</sup>(R<sup>5</sup>)(R<sup>6</sup>) and the like, wherein R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are independently alkyl, phenyl, alkyl ether, or phenyl ether,  
 15 preferably at least two of R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> being a hydrolyzable group, more preferably two of which are alkyl ether, wherein alkyl is preferably methyl or ethyl. A plurality of silyl groups can be condensed; for example, an organopolysiloxane such as -Si(R<sup>4</sup>)<sub>2</sub>-O-Si(R<sup>5</sup>)<sub>2</sub>R<sup>6</sup>, wherein R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are independently alkyl.

Preferred monomers are methyl methacrylate, ethyl methacrylate, propyl  
 20 methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha methyl styrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional  
 25 methacrylate, acrylates and styrene selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers),  
 30 diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-tert-butyl methacrylamide, N-n-butyl methacrylamide, N-methyl-ol methacrylamide, N-ethyl-ol methacrylamide, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methyl-ol acrylamide, N-ethyl-ol acrylamide, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), alhamethylvinyl benzoic acid (all isomers), diethylamino  
 35 alhamethylstyrene (all isomers), para-methylstyrene, p-vinyl benzene sulfonic acid, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate,

- tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethyl-silylpropylmethacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate,
- 5 diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl
- 10 acrylate, vinyl acetate, and vinyl butyrate, vinyl chloride, vinyl fluoride, vinyl bromide.

In a preferred process, (ii) is selected where Q, -X<sub>2</sub>C-CH<sub>2</sub>- and Z are independently selected from one or more of the following:

- Q = H, methyl, ethyl, butyl (all isomers), cyclohexyl, methoxy, ethoxy, propoxy, butoxy (all isomers), phenoxy, acetate, propionate, butyrate (all isomers),
- 15 benzoate, carboxylate, chlorine, bromine, fluorine, iodine, nitrile, amide, N-methylamide, N-ethylamide, N-propylamide, N,N-dimethylamide, N,N-diethylamide, N,N-dibutylamide, N-methyl-N-ethylamide, carboxylate ester of methyl, ethyl, propyl, butyl (all isomers), benzyl, phenyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-hydroxy-butyl (all isomers), 3-
- 20 hydroxybutyl (all isomers), 2-hydroxybutyl, 3-trimethoxysilylpropyl, 3-triethoxysilylpropyl, 3-tributoxy-silylpropyl, 3-tri(isopropoxy)silylpropyl, 2-aminoethyl, 3-amino-propyl, 2-aminopropyl, 4-aminobutyl (all isomers), 3-aminobutyl (all isomers), 2-aminobutyl (all isomers), 2-epoxypropyl, or 3-epoxypropyl;
- 25 -X<sub>2</sub>C-CH<sub>2</sub>- = derived from one or more of the following monomers: methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, styrene, alpha methyl styrene, glycidyl methacrylate, 2-hydroxyethyl
- 30 methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), diethylaminoethyl methacrylate, triethyleneglycol methacrylate, N-tert-butyl methacrylamide, N-n-butyl methacrylamide, N-methyl-ol methacrylamide, N-ethyl-ol methacrylamide, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl
- 35 methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate,

- dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), diethylaminoethyl acrylate, triethyleneglycol acrylate, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methyl-ol acrylamide, N-ethyl-ol acrylamide, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), p-vinyl benzene sulfonic acid, para-methylstyrene, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, or vinyl butyrate;
- 5           Z = H, SR<sup>1</sup>, S(O)R, S(O)<sub>2</sub>R, R<sup>2</sup>, or R<sup>3</sup>;
- 10           R = methyl, ethyl, propyl, n-butyl, tert-butyl, isobutyl, phenyl, benzyl, 2-phenylpropyl, trimethoxysilylpropyl, tributoxysilylpropyl, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 2-epoxypropyl, 2-aminoethyl, 2-aminopropyl, methoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxy-propyl, or
- 15           heptafluoropropyl;
- 20           R<sup>1</sup> = hydrogen, methyl, ethyl, propyl, n-butyl, tert-butyl, isobutyl, phenyl, benzyl, 2-phenylpropyl, trimethoxysilylpropyl, tributoxysilylpropyl, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 2-epoxypropyl, 2-aminoethyl, 2-aminopropyl, methoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxypropyl, or
- 25           heptafluoropropyl;
- 30           R<sup>2</sup> = 2,4-dimethylpentanenitrile, 2-methylbutanenitrile, 2-methylpropanenitrile, cyclohexanecarbonitrile, 4-cyanopentanoic acid, N,N'-dimethyleneisobutyramidine, N,N'-dimethyleneisobutyramidine hydrochloride, 2-amidinopropane, 2-amidinopropane hydrochloride, 2-methyl-N-[1,1-bis(hydroxymethyl)ethyl] propionamide, 2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2-methyl-N-(2-hydroxyethyl) propionamide, isobutyramide hydrate, hydroxyl, or sulfate;
- 35           R<sup>3</sup> = 1,1-bis(carboethoxy)ethyl, 1,1-bis(carbomethoxy)ethyl, bis(carboethoxy)methyl, bis(carbomethoxy)methyl, 1-carboethoxy-1-phenyl ethyl, 1-carbomethoxy-1-phenyl ethyl, chlorine, bromine, fluorine, iodine, 1-methyl-1-[carbo(2-epoxypropoxy)]ethyl, 1-methyl-1-[carbo(2-hydroxyethoxy)]ethyl, 1-methyl-1-[carbo(4-hydroxy-butoxy)]ethyl, 1-methyl-1-[carbo(2-aminoethoxy)]ethyl, 1-methyl-1-[carbo(3-trimethoxysilylpropoxy)]ethyl, 1-

methyl-1-[carbo(3-triethoxysilylpropoxy)]ethyl, 1-methyl-1-[carbo(3-dimethoxyethoxysilylpropoxy)]ethyl, 1-methyl-1-[carbo(2-methoxyethoxy)]ethyl, (N,N-di-methylamino)(cyano)methyl, N,N-dimethylamino-(benzo)methyl, thiomethyl(cyano)methyl, or thioethyl(cyano)methyl.

5

In a preferred process, (iii) is derived from one or more of the following initiators: 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-cyanpentanoic acid), 1,1'-azobis(cyclohexene-carbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dichloride, 2,2'-azobis(2-amidinopropane) dichloride, 2,2'-azobis(N,N'-dimethyleneisobutyramide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl) ethyl] propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(isobutyramide) dihydrate, t-butyl-peroxyacetate, t-butylperoxybenzoate, t-butylperoxyoctoate, t-butylperoxyneodecanoate, t-butylperoxyisobutyrate, t-amylperoxypivalate, t-butylperoxypivalate, cumene hydroperoxide, dicumyl peroxide, benzoyl peroxide, potassium persulfate, ammonium persulfate.

20

#### DETAILS OF THE INVENTION

Compound (2) can be prepared by several methods. Two non-restrictive examples of convenient methods of preparing compounds of structure (2) are by free radical polymerization in the presence of cobalt transfer agents or organic transfer agents that are capable of chain transfer by addition fragmentation. Cobalt chain transfer agents represent a broad class of complexes some of which are described in U.S. Patent No. 4,694,054, U.S. Patent No. 4,680,352, U.S. Patent No. 4,722,984, and WO 87/03605.

Organic chain transfer agents include allylic sulfides, allylic bromides, vinyl terminated methacrylic oligomers (dimers, trimers, etc or distributions), a-methylstyrene dimer and related compounds. Other methods of preparation are also possible.

Said compounds of structure (2) can also be a block copolymer of general structure (1) and the process can then be used to form tri- or multiblock copolymers.

Substituent Q of (1) and (2) is chosen to convey appropriate reactivity to the double bond in radical polymerization of the desired monomer or monomers under polymerization conditions. It should preferably be aryl, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, or



CONR<sub>2</sub> in the case of activated monomers (e.g. styrene, acrylics) or H, R, OR, O<sub>2</sub>CR, or halogen in the case of non activated monomers (e.g. vinyl acetate, vinyl chloride).

The substituents Q and Z can also be chosen so as to introduce any required end-group functionality into the polymer (1). These end groups can be the same or different and are chosen such that the final polymer is a telechelic polymer. Suitable end groups are those compatible with free radical polymerization and include epoxy, hydroxy, carboxylic acid, carboxylic ester.

Monomers, CH<sub>2</sub>=C<sub>UV</sub>, as used herein include acrylic, methacrylic and styrenic monomers, mixtures thereof, and mixtures of these monomers with other monomers. As one skilled in the art would recognize, the choice of comonomers is determined by the steric and electronic properties of the monomer. The factors which determine copolymerizability of various monomers is well documented in the art.

When U and/or X= hydrogen, the use of reaction temperatures above 100°C has been found to favor block copolymer formation.

The process is compatible with forming (2) and the polymer (1) sequentially in a "one-pot" procedure. In this case, it is important to destroy residual transfer agent remaining from the synthesis of (2). For compounds (2) prepared in the presence of cobalt catalytic chain transfer agents, the use of potassium persulfate, a peroxide or similar reagent deactivates any cobalt chain transfer agent remaining from the compound (2) preparation.

The length of the -(CXY-CH<sub>2</sub>)<sub>n</sub>- is determined by the molecular weight of (2). Unreacted (2) will constitute a contaminant. The conversion level of (2) will define the purity of (1). The higher the conversion of (2) the higher the purity of (1).

To obtain narrow dispersity in the final polymer, reaction conditions are selected such that polymerization in the absence of (2) gives molecular weights substantially higher (at least 5-fold) than in the presence of (2). In the same manner, to obtain high block purity in the block copolymer synthesis, reaction conditions are selected such that polymerization in the absence of compound (2) gives molecular weights substantially higher (at least 5-fold) than in the presence of compound (2).

With this as a guide, the control of the molar amount of free radicals (iii) at any given conversion of (i) will determine how much polymer containing (i) and not (2) is formed. One can minimize the number of free radicals, via initiators, in the reaction media during the polymerization so that bimolecular termination reactions, or radical-radical reactions, are minimized. These reactions produce polymers that are undesirable when one is interested in narrow dispersity polymers or substantially pure block copolymers. Increasing the moles of (ii) in the presence of (iii) will enhance the transfer reaction which is necessary to produce block, telechelic polymers and homopolymers of narrow molecular weight dispersity. In like fashion, reducing the

molar amount of monomer (i) in the reactor at any given time at any given conversion of (iii), will provide additional control thus assuring uptake of (ii) as a transfer agent. Slow, incremental uptake of (i) under conditions which optimize chain transfer contribute to narrow polydispersity. The present invention allows preparation of

5 homo- and copolymers with substantially narrower polydispersity than can be prepared by conventional free radical polymerization. Polymers with polydispersity <1.5 are not available using conventional free radical polymerization technology. The discovered interrelationship of (a) to (d) allows preparation of polymers with

10 polydispersities below 1.7 and even less than 1.5.

15 The process can be successfully conducted by bulk, solution, suspension or emulsion polymerization. However, bearing in mind the above-mentioned condition, a preferred process for forming high molecular weight block copolymers is by emulsion or dispersion polymerization techniques. Emulsion polymerization typically offers very high molecular weights for polymerization carried out in the absence of

20 compound (2). As a consequence, it is possible to prepare high molecular weight, high purity block copolymers with narrow polydispersity. Other advantages of emulsion polymerization over solution or bulk polymerization are faster polymerization times, high conversions, avoidance of organic solvents, and low chain transfer to water.

25 The present process offers significant advantages over other processes for preparing block or narrow polydispersity polymers based on conventional living polymerization techniques (e.g. cationic, anionic, coordination or group transfer polymerization). Advantages include compatibility with monomers with active hydrogens (for example, methacrylic acid, 2-hydroxyethyl methacrylate, etc.), or

30 reactive functionality (for example, glycidyl methacrylate), the use of protic media (for example, isopropanol, water), and use of inexpensive commercial grade monomers.

The success of block copolymerization via the emulsion process depends on the compatibility of the monomer(s) and compound (2). The polymerization of hydrophobic monomers (e.g. butyl methacrylate) and moderately hydrophobic

35 compounds (2) (e.g. methyl methacrylate), or moderately hydrophobic monomers with hydrophilic compounds (2) (e.g. methacrylic acid) can be successfully carried out.

Emulsion polymerization of hydrophobic monomers (for example, styrene, butyl methacrylate, etc.) in the presence of water-soluble compounds (2) may lead to product contaminated with homopolymer of the hydrophobic monomers. In these

40 circumstances, addition of appropriate cosolvents (for example, 2-butoxyethanol) to the emulsion polymerization medium gives improved yields of block copolymer.

Changing the hydrophobic-hydrophilic balance in the compound (2) also gives improved yield of block copolymer. For example, block copolymers based on

hydrophobic monomers (for example, styrene, butyl methacrylate, etc.) and 60:40 methyl methacrylate-co-methacrylic acid compounds (2) are readily synthesized in high yield and purity by emulsion polymerization.

The low cost of the process means that purification of the block copolymer can be economically viable when this is necessary or desirable. Thus, lower yields of block copolymers can be tolerated than with other synthetic methods.

The process of the invention is further illustrated by the following Examples in which these abbreviations are used:

	EHMA	2-ethylhexyl methacrylate
10	n-BA	n-butyl acrylate
	BAC	butyl acetate
	EAC	ethyl acetate
	GMA	glycidyl methacrylate
	n-BMA	n-butyl methacrylate
15	t-BMA	tert-butyl methacrylate
	i-BMA	iso-butyl methacrylate
	BzMA	benzyl methacrylate
	EMA	ethyl methacrylate
	HEMA	hydroxyethyl methacrylate
20	iPrOH	2-propanol
	MAA	methacrylic acid
	MEK	methylethyl ketone
	MMA	methyl methacrylate
	PhMA	phenyl methacrylate
25	S	styrene
	pMS	p-methylstyrene
	CHMA	cyclohexyl methacrylate
	VAZO 52	2,2'-azobis(2,4dimethylpentanenitrile)
	VAZO 88	1,1'-azobis(cyclohexanecarbonitrile)
30	WAKO VA044	2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride
	iprCo(III)DMG	[bis[m-[(2,3-butanedione dioximato)(2-)-O:O']] tetrafluorodiborato (2-) -N,N',N'',N'''] (1- methylethyl) (aqua) cobalt
35	MeCo(III)DEG	[bis[m-[(2,3-hexanedione dioximato)(2-)-O:O']] tetrafluorodiborato (2-) -N,N',N'',N'''] (methyl) (aqua) cobalt

EXAMPLES 1-9Methacrylic Acid Block Copolymers by Emulsion Polymerization

5 This is the basic recipe for surfactantless emulsion polymerization and illustrates the use of block copolymers as latex stabilizers.

Preparation of Methacrylic Acid-*block*-Methyl Methacrylate

	Water	75.0 g
	NaHCO <sub>3</sub>	0.151 g
10	MAA <sub>12</sub> - <i>block</i> -BMA <sub>4</sub>	0.376 g
	MAA Compound 2 ( <sup>1</sup> H NMR: $\bar{M}_n$ 950)	10.07 g
	MMA	1.00 g
	4,4' azobis(4-cyanopentanoic acid)	0.140 g
	MMA	10.0 g

15

The water was degassed in a multi-neck, 250 mL reactor under nitrogen for 20 min. The solution was heated to 85°C. The sodium bicarbonate, block copolymer and MAA Compound 2 were added, and the solution was degassed for a further 10 min. The initiator and a portion of the MMA (1.00 g) were added as single shots and the remaining MMA added as a feed over 90 min. The reaction mixture was held at 85°C for a further 90 min.

20

GPC:  $\bar{M}_n$  3010,  $\bar{M}_w$  4270; Dispersity 1.42.

25 The yield of block copolymer vs. 'homopolymer' formed by emulsion polymerization depends on the relative hydrophobicity of the compound (2) and monomer. The examples given in the table show that, for systems where this is a problem (e.g. MAA-*block*-BMA), the yield of block copolymer are improved by use of an appropriate cosolvent.

Table 1. Methacrylic Acid Block Copolymers by Emulsion Polymerization<sup>a</sup>

Example	Monomer	Co-solvent	% block <sup>b</sup>
1	MMA	none	100
2	EMA	none	70
5	3	nBMA	43
4	nBA	none	20
5	MMA/BMA 1:2	none	30
6	MMA/BMA 2:1	none	60
7	MMA/BMA triblock (1:2)	none	60
10	8	nBMA	10 % 2-ethoxyethanol <sup>c</sup>
9	nBMA	10 % 2-butoxyethanol <sup>c</sup>	100

<sup>a</sup>Methacrylic acid macromonomer (<sup>1</sup>H NMR:  $M_n$  950).<sup>b</sup>Estimated by GPC. Remainder is 'B block' homopolymer<sup>c</sup>Feed time increased to 270 min

15

EXAMPLES 10 - 14

## Methacrylate Ester Based Block Copolymers

Preparation of Phenyl Methacrylate-*block*-Butyl Methacrylate

## 20 A. Preparation of PhMA compound (2)

	Water	75 g
	SDS (1 wt% aq. solution)	3 g
	4,4'-azobis(4-cyanopentanoic acid)	0.140 g
Monomer Shot:	PhMA	3.5 g
25	MeCo(III)DEG	15.0 mg
Monomer Feed:	PhMA	31.7 g
	MeCo(III)DEG	11.8 mg

30 The water, initiator and SDS were combined and degassed under nitrogen in a multi-necked 250 mL reactor. The mixture was heated to 80°C and the monomer shot added immediately. The monomer feed was added over 90 min. The temperature was increased to 85°C and held for a further 90 min.

GPC:  $\bar{M}_n$  1100  $\bar{M}_w$  2400; Dispersity 2.18.

## B. Preparation of PhMA-block-BMA

	PhMA compound (2) latex (33% solids) <sup>a</sup>	30 g
	Initiator Feed: $K_2S_2O_8$ (0.2 wt% aq. solution)	56.8 mL
	Monomer Feed: nBMA	60 g
5	a. 0-90 min 0.25 mL/min	
	b. 90-180 min 0.50 mL/min	

<sup>a</sup>from Part A

- 10 The PhMA compound (2) latex ( $\bar{M}_n$  1100,  $\bar{M}_w$  2400; Dispersity 2.18) was heated to 80°C in a multi-neck 250 mL reactor under nitrogen for 50 min. The initiator and monomer feeds were added concurrently over 180 min. Portions of SDS (1 g of a 10 wt% aqueous solution) were added hourly during the monomer addition. After monomer addition was complete the reaction temperature was increased to 85°C and held for a further 90 min.
- 15 GPC:  $\bar{M}_n$  14500,  $\bar{M}_w$  33400; Dispersity 2.30

Table 2. Methacrylic Ester Block Copolymers prepared by Emulsion Polymerization

Example	Compound 2	Monomer	Block Composition <sup>a</sup>	M <sub>n</sub> <sup>b</sup>	Dispersity
10	PhMA	nBMA	(PhMA) <sub>7</sub> /(nBMA) <sub>94</sub>	14500	2.30
11	MAA	MMA	(MAA) <sub>11</sub> /(MMA) <sub>14</sub> <sup>c</sup>	3010	1.42
12	MAA	nBMA <sup>d</sup>	(MAA) <sub>11</sub> /(nBMA) <sub>22</sub>	4030	2.31
13	MMA	nBMA	(MMA) <sub>19</sub> /(nBMA) <sub>46</sub>	6700	1.19
14	tBMA	nBMA	(tBMA) <sub>17</sub> /(nBMA) <sub>24</sub>	5780	1.33

<sup>a</sup>estimated from GPC<sup>b</sup>GPC (polystyrene equivalents)<sup>c</sup>estimated from <sup>1</sup>H NMR<sup>d</sup>10 % 2-butoxyethanol (see Table 1)

30

EXAMPLES 15 - 19Narrow Polydispersity Polymers

- These examples illustrate the preparation of a polymer of relatively narrow polydispersity by emulsion polymerization. Polydispersities (> 1.5) are narrower than expected by normal polymerization with chain transfer (2.0). The polydispersity typically narrows with increased monomer addition as shown in Table 3. To achieve narrow polydispersities it is necessary to control the rate of monomer addition to maintain relatively high % solids (typically in range 70-95%) and a constant monomer concentration.
- 35

Preparation of Methyl Methacrylate-*block*-Butyl Methacrylate

## A. Preparation of MMA compound (2)

	Water	150 g
	SDS (3 wt% aq. solution)	6 g
5	4,4'-azobis(4-cyanopentanoic acid)	0.280 g
Monomer Shot:	MMA	7 g
	MeCo(III)DEG	5 mg
Monomer Feed:	MMA	63.4 g
	MeCo(III)DEG	2.3 mg

10

The water, initiator and SDS were combined and degassed under nitrogen in a multi-necked 250 mL reactor. The mixture was heated to 80°C and the monomer shot added immediately. The monomer feed was added over 90 min. The temperature was increased to 85°C and held for a further 90 min.

15 GPC:  $\bar{M}_n$  3500  $\bar{M}_w$  5600; Dispersity 1.61.  
 $^1\text{H NMR}$ :  $\bar{M}_n$  3100

B. Preparation of MMA-*block*-BMA

	MMA compound (2) latex (33 % solids) <sup>a</sup>	30 g
Initiator Feed:	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0.4wt % aq. solution)	28.4 mL/90 min
20 Monomer Feed:	nBMA	20 g/90 min

<sup>a</sup>from Part A

25 The MMA compound (2) was heated to 80°C in a multi-neck 250 mL reactor under nitrogen for 30 min. The initiator and monomer feeds were added concurrently over 90 min. The monomer and initiator additions were then repeated until a total of 100 g BMA was added. Portions of SDS (1 g of a 3 wt% aqueous solution) were added hourly during the monomer addition. After monomer addition was complete the reaction temperature was increased to 85°C and held for 90 min.

30 GPC:  $\bar{M}_n$  23800,  $\bar{M}_w$  33100; Dispersity 1.39

Table 3: Variation in Molecular Weight and Polydispersity with Monomer Addition  
(compound (2) = PMMA)

Example	Monomer	monomer (g)	$M_n^a$	$M_w/M_n$	$M_n(\text{calc})^b$
5	BMA	0	3500 (3100 <sup>c</sup> )	1.6	
		20	8300 (9700)	1.5	9300
		40	13200 (15400)	1.4	15500
		60	17700 (20100)	1.3	21700
		80	20000 (23600)	1.3	27900
		100	23800 (28100)	1.4	34500
10	MMA	0	1850 (2100)	1.5	
		15.8	3800 (4320)	1.4	4800
		24.2	4770 (5300)	1.4	6300
		31.6	5740 (6500)	1.5	7700
		63.1	9790 (11200)	2.7	13500
20	MMA	0	3260 (3700)	1.5	
		11.8	9900 (11300)	1.4	10900
		19.0	13700 (15700)	1.5	15600
		35.2	22100 (25300)	1.6	26200
		52.9	31300 (35900)	1.8	37700
		65.8	37600 (43200)	2.1	46100
25	BMA	0	2000 <sup>c</sup>	1.6	
		25.7	6700 (7900)	1.2	8000
		33.6	8400 (9900)	1.2	9900
		50.3	12300 (14500)	1.2	13800
		59.8	14900 (17600)	1.2	16100
		67.1	16800 (19800)	1.2	17800
30	BMA	88.2	18400 (21700)	1.4	22800
35	EHMA	0	2050 <sup>c</sup>	1.7	
		20	4900	1.5	4800
		40	7100	1.4	7600
		60	10500	1.3	10400
		78	11800	1.3	12900

<sup>a</sup>GPC molecular weight in polystyrene equivalents (values obtained by applying universal calibration in parentheses). Numbers rounded to nearest hundred.



<sup>b</sup>Mn = ([monomer]/[compound (2)] x monomer Mn) + compound (2) Mn. Discrepancies between calculated and found Mn may reflect precision of compound (2) concentration.

<sup>c</sup>Mn of PMMA.

5

## EXAMPLES 20 - 21

### Triblock Copolymers

These examples illustrate the synthesis of an ABA triblock copolymer. The procedure is compatible with a 'one-pot' operation.

#### 10 Preparation of MMA-*block*-BMA-*block*-MMA.

##### A. Preparation of MMA-*block*-BMA

		MMA compound (2) latex <sup>c</sup>	30 g
		SDS (3 wt% aq. solution)	1 g
Initiator Feed:	(0.316 mL/min)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0.36wt % aq. solution)	40.8 g
15 Monomer Feed:	(0.218 mL/min)	nBMA	25.2 g

(<sup>c</sup>ca. 32 % solids,  $\bar{M}_n$  2040, Dispersity 1.51, prepared with iPrCo(III)DMG procedure similar to Example 15, part A)

20 The MMA compound (2) latex and SDS was placed in a multi-neck 250 mL reactor, degassed under vacuum, then heated to 80°C under nitrogen. The initiator and monomer feeds were added concurrently over 130 min. After monomer addition was complete the reaction was held at 80°C for 90 min. A shot of surfactant was added (1g of 3 wt% aq. solution of SDS) at 60 min intervals.

25 GPC:  $\bar{M}_n$  6650,  $\bar{M}_w$  8400; Dispersity 1.26.

##### B. Preparation of MMA-*block*-BMA-*block*-MMA

		MMA- <i>block</i> -BMA compound (2) latex <sup>c</sup>	30 g
		SDS (3 wt% aq. solution)	1 g
Initiator Feed:	(0.316 mL/min)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0.36wt % aq. solution)	21.5 g
30 Monomer Feed:	(0.119 mL/min)	MMA	7.5 g

(<sup>c</sup>ca. 32 % solids, from part A)

35 The MMA compound (2) latex and SDS was placed in a multi-neck 250 mL reactor, degassed under vacuum, then heated to 80°C under nitrogen. The initiator and monomer feeds were added concurrently over 68 min. After monomer addition was complete the reaction was held at 80°C for 90 min. A shot of surfactant was

added (1 g of 3wt % aq. solution of SDS) at 60 min intervals. The conversion based on % solids was 98%.

GPC:  $\bar{M}_n$  12660,  $\bar{M}_w$  16590; Dispersity 1.35

5

Table 4. Emulsion Triblock Copolymers

Example	Step/Monomer	Macromonomer			Block	
		Composition	$M_n^a$	Dispersity	$M_n^a$	Dispersity
20	1:BMA	MMA	2040	1.51	6650	1.26
	2: MMA	MMA- <i>block</i> -BMA	6650	1.26	12660	1.35
21	1:BMA	MMA	3500	1.62	23800	1.39
	2:MMA	MMA- <i>block</i> -BMA	23800	1.39	26200	1.52

<sup>a</sup>GPC (polystyrene equivalents)

### EXAMPLE 22

#### 'One Pot' Synthesis of (MMA-co-MAA)-*block*-BMA

10        These examples illustrate a 'one-pot' synthesis of compound (2) and block copolymer by emulsion polymerization.

#### A. Preparation of MMA-co-MAA compound (2)

15	Solution 1:	Water	120.00 g
		MAA- <i>block</i> -BMA	2.87 g
20	Feed 1:	iprCo(III)DMG	7.5 mg
		WAKO VA-044	0.33 g
		MMA	4.0 g
25	Feed 2:	MMA	42.14 g
		iprCo(III)DMG	15.0 mg
	a. 0-20 min	MAA	15.60 g
			0.137 mL/min
			0.276 mL/min
	b. 20-40 min		0.356 mL/min
	c. 40-60 min		

The MAA-*block*-BMA(stabilizer/surfactant)/water mixture was heated to 58°C in a multi-necked 500 mL reactor under nitrogen for 30 min. Solution 1 was

added and the monomer feeds were added concurrently over 60 min. On completion of the monomer addition the reaction temperature was increased slowly to 80°C.

GPC:  $\bar{M}_n$  880,  $\bar{M}_w$  1400; Dispersity 1.59

B. Preparation of (MMA-co-MAA)-*block*-BMA

5	MMA/MAA Compound 2 latex	from part A
	MAA- <i>block</i> -BMA	0.288 g
	water	9.3 g
	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.224 g
10	Initiator Feed: K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (1.25% aq. solution)	28.4 mL
	Monomer Feed: nBMA	12 g

The MMA/MAA compound (2) latex from Part A was held at 80°C for 40 min under nitrogen. MAA-b-BMA (surfactant) was added and the reactor degassed for a further 20 min. The initiator was then added as a single shot. The initiator and monomer feeds were added concurrently over 90 min. On completion of the feeds the reaction temperature was held at 80°C for 30 min and then increased to 85°C for 90 min.

20 GPC:  $\bar{M}_n$  3090,  $\bar{M}_w$  5370; Dispersity 1.74

### EXAMPLES 23 - 36

#### Synthesis of block copolymers in solution

25 The following examples illustrate the synthesis of block copolymers from methacrylate compounds (2).

Preparation of (MMA-co-MAA)-*block*-BMA

	MMA-co-MAA Compound 2 ( $\bar{M}_n$ 1031; Dispersity 1.53)	10.0 g
	xylene	30.0 g
30	t-butyl peroxybenzoate	0.1 g
	Feed One: n-butyl methacrylate	10.0 g
	Feed Two: t-butyl peroxybenzoate	0.2 g
35	xylene	10.0 g

The compound (2) and initiator were dissolved in the solvent and heated to reflux under nitrogen. The monomer and initiator feeds were added concurrently over 180 min. After completion of the feeds, the mixture was heated under reflux for a further 180 min.

- 5 Conversion: > 95%.  
GPC:  $\bar{M}_n$  1890,  $\bar{M}_w$  2640; Dispersity 1.40

Table 5. Solution Block Copolymers from Methacrylate Monomers

Ex.	Mon.	R <sup>1</sup>	Solvent	Compound (2)			Block	
				Composition	$\bar{M}_n$	Disp.	$\bar{M}_n$	Disp.
23	nBMA	46	iPrOH	MAA <sub>9</sub>	880 <sup>c</sup>	—	2400 <sup>d</sup>	1.50
24	nBMA	46	iPrOH	MAA <sub>9</sub>	880 <sup>c</sup>	—	3030 <sup>d</sup>	1.53
25	nBMA	46	EtOH	MAA <sub>9</sub> -co-BMA <sub>5</sub>	1620 <sup>d</sup>	2.2	2320 <sup>d</sup>	2.47
26	BzMA	47	iPrOH	MMA <sub>20</sub> -co-MAA <sub>5</sub> <sup>c</sup>	2460 <sup>b</sup>	1.23	6020 <sup>b</sup>	1.63
27	BzMA	47	iPrOH	MMA <sub>10</sub> -co-MAA <sub>5</sub>	1600 <sup>b</sup>	1.71	5320 <sup>b</sup>	1.80
28	BzMA	47	iPrOH	BMA <sub>10</sub> -co-MAA <sub>5</sub>	2040 <sup>b</sup>	2.56	6070 <sup>b</sup>	1.69
29	BzMA	47	iPrOH	EHMA <sub>10</sub> -co-MAA <sub>5</sub>	1900 <sup>b</sup>	1.62	4020 <sup>b</sup>	1.61
30	MMA-BMA <sup>f</sup>	46	iPrOH	MAA <sub>9</sub> -co-BMA <sub>5</sub>	1620 <sup>d</sup>	2.2	2930 <sup>d</sup>	1.81
31	MMA-BMA <sup>f</sup>	46	iPrOH	MAA <sub>9</sub> -block-BMA <sub>5</sub>	2400 <sup>d</sup>	1.50	2790 <sup>d</sup>	1.85
32	MMA-BMA <sup>f</sup>	46	iPrOH	MAA	860 <sup>c</sup>	—	3050 <sup>b</sup>	1.64
33	MMA	46	iPrOH	HEMA <sub>11</sub>	1550 <sup>d</sup>	—	3620 <sup>d</sup>	1.83
34	MMA	48	xylene	MMA-co-MAA	1031 <sup>b</sup>	1.53	2640 <sup>b</sup>	1.40
35	nBMA	23	xylene	MMA	890 <sup>b</sup>	1.97	1340 <sup>b</sup>	1.78
36	MMA		BAC	MMA-co-MAA	1031 <sup>b</sup>	1.53	2068 <sup>b</sup>	1.38

<sup>a</sup>R = "recipe", similar to that of the Example referred to by number. All reactions were carried out at reflux. Conversions were typically >85%

<sup>b</sup>GPC (polystyrene equivalents).

<sup>c</sup>from NMR.

<sup>d</sup>GPC (PMMA equivalents).

<sup>e</sup>Compound (2) prepared by emulsion polymerization.

<sup>f</sup>1:1 mole ratio comonomers.

### EXAMPLES 37-45

#### Synthesis of block copolymers in solution

For monosubstituted monomers higher block purity is found when higher reaction temperatures are used. At low temperatures graft copolymer formation may

dominate. Xylene and butyl acetate or other solvents with similar boiling point are preferred for block syntheses with monosubstituted monomers.

Preparation of (MMA-co-MAA)-block-BA

5	Compound 2 ( $\bar{M}_n$ 1031; Dispersity 1.53)	8.88 g
	Xylene	37.8 g
	t-butyl peroxybenzoate	0.1 g
	n-butyl acrylate	1.6 g
10	Feed:	
	t-butyl peroxybenzoate	0.16 g
	n-butyl acrylate	9.5 g

The compound (2) and initiator were dissolved in the solvent and heated to reflux under nitrogen. The monomer and initiator feed was added over 180 min. After completion of the feeds, the mixture was heated under reflux for a further 180 min.

Conversion: > 95%.

GPC:  $\bar{M}_n$  1760,  $\bar{M}_w$  2710; Dispersity 1.54

Table 6. Solution Block Copolymers from Monosubstituted Monomers

Ex.	Mon.	R <sup>a</sup>	Solvent	Compound (2)			Block		
				Composition	$\bar{M}_n$	Disp.	$\bar{M}_n$	Disp.	Purity <sup>b</sup>
37	BA	37	xylene	MMA-co-MAA	1031 <sup>d</sup>	1.53	1760 <sup>d</sup>	1.54	>80%
38	BA	46	iPrOH	MAA <sub>9</sub>	880 <sup>c</sup>	-	2620 <sup>d</sup>	2.45	>90% <sup>e</sup>
39	BA	37	BAC	MMA-co-MAA	1031 <sup>d</sup>	1.53	2683 <sup>d</sup>	1.76	>80%
40	BA	23	xylene	MMA	840 <sup>d</sup>	1.97	2100 <sup>c</sup>	2.05	>70%
41	S	46	iPrOH	MAA	880 <sup>c</sup>	-	1890 <sup>d</sup>	2.10	>90% <sup>e</sup>
42	S	37	BAC	MMA	1640 <sup>d</sup>	2.22	2530 <sup>d</sup>	2.37	>70%
43	S	37	BAC	nBMA	1030 <sup>d</sup>	2.04	4650 <sup>d</sup>	2.79	>70%
44	S	37	BAC	tBMA	2620 <sup>d</sup>	2.62	3620 <sup>d</sup>	2.20	>70%
45	S	23	xylene	MMA	840 <sup>d</sup>	1.97	1780 <sup>c</sup>	2.04	>70%

<sup>a</sup>R = "recipe", similar to that of the Example referred to by number. All reactions were carried out at reflux. Conversions were typically >85%

<sup>b</sup>from comparison of GPC and NMR molecular weights

<sup>c</sup>from NMR

<sup>d</sup>GPC (polystyrene equivalents)

<sup>e</sup>evidence of reduced block copolymer formation

EXAMPLE 46Preparation of MAA-*block*-BMA

	methacrylic acid Compound 2°	15 g
	isopropanol	62.8 g
5	azobis(isobutyronitrile)	0.32 g
	acetone	2 mL

Feed: n-butyl methacrylate 14.3 g

°(MAA compound (2) having  $\bar{M}_n$  1040 and Dispersity 1.80).

10

The compound (2) and solvent were heated to reflux (ca. 80°C) under nitrogen. The initiator (dissolved in acetone) was added as a single shot and the monomer feed added over 180 min. After 90 min the initiator was replenished (0.16 g AIBN/ 1 mL acetone). After completion of feed the mixture was heated under reflux for a further 150 min.

15

Conversion: > 87 %

GPC:  $\bar{M}_n$  2580,  $\bar{M}_w$  4900; Dispersity 1.90.

20

EXAMPLE 47

This example shows the successful 20-fold scale up of Example 46.

Preparation of MAA-*block*-BMA

	methacrylic acid compound (2)°	200 g
	isopropanol	1000 mL
25	azobis(isobutyronitrile)	4.01 g

Feed: (1 mL/min) n-butyl methacrylate 326.1 g

°( $M_n$  from NMR 1204).

30

The compound (2) and solvent were placed in a 2 L multinecked flask equipped with mechanical stirrer, degassed, and heated to reflux (ca. 80°C) under nitrogen. The initiator was added as a single shot and the monomer feed commenced. At ca. 90 min intervals the initiator was replenished (2 g shots of AIBN). On completion of feed, the mixture was heated under reflux for a further 150 min.

35

Conversion: > 95 %

GPC:  $\bar{M}_n$  3532,  $\bar{M}_w$  5102; Dispersity 1.45

EXAMPLE 48

5 This example illustrates the synthesis of hydrophilic-hydrophobic block copolymers based on methacrylate ester-methacrylic acid copolymers by solution polymerization.

## A. Preparation of MAA-co-BMA Compound (2)

	Isopropanol	20.06 g
	MAA	1.21 g
10	nBMA	3.86 g
	2,2'-azobis(2-butanenitrile)	0.25 g
	Shot:	IPrCo(III)DMG (0.35 wt% in isopropanol)
		7.5 mL
		0.140 g
15	Feed 1: (0.128 mL/min)	IPrCo(III)DMG (0.33 wt% in isopropanol)
		30.7 mL
	Feed 2: (0.224 mL/min)	MAA
		11.40 g
		nBMA
		37.83 g

20

The isopropanol was degassed under nitrogen in a multi-necked 250 mL reactor equipped with a mechanical stirrer. The monomers were then added and the mixture and heated to reflux (80°C). The shot was then added and the feeds added over 240 min by syringe pumps. Further initiator (0.125 g) was added at 120 min and 25 240 min. On completion of the feeds the temperature was held at 80°C for 90 min. The conversion based on % solids was > 85%.

NMR composition: MAA<sub>5</sub>-co- BMA<sub>11</sub>GPC(PMMA equivalents):  $\bar{M}_n$  2040,  $\bar{M}_w$  5210; Dispersity 2.56B. Preparation of MAA-co-BMA-*block*-Benzyl Methacrylate

30	MAA-co-nBMA compound (2)	
	solution <sup>o</sup> (60 wt% in isopropanol)	30.0 g
	isopropanol	9.98 g
	2,2'-azobis(2-butanenitrile)	0.092 g
35	Feed: (0.202 mL/min)	BzMA
		18.0 g
		isopropanol
		15.0 g

<sup>o</sup>from Part A

The compound (2) solution and isopropanol were placed in a multi-neck 250 mL reactor fitted with a mechanical stirrer, degassed then heated to 80°C under nitrogen. The initiator was added and the monomer feed commenced and added over 180 min by syringe pump. Further aliquots of initiator were added at 90 min (0.049 g) and 180 min (0.087 g). The reaction was held at 80°C for a further 90 min. The conversion based on % solids was >94%.

NMR composition: MAA<sub>3</sub>-co- BMA<sub>11</sub>-block-BzMA<sub>20</sub>

GPC(PMMA equivalents):  $\bar{M}_n$  6070,  $\bar{M}_w$  9770; Dispersity 1.61

10

EXAMPLE 49

This example illustrates the synthesis of a hydrophilic-hydrophobic block copolymer based on HEMA by solution polymerization.

## A. Preparation of Hydroxyethyl Methacrylate Compound (2)

15	Water	75 g
	Shot:	
	HEMA	3.5 g
	iPrCo(III)DMG	4 mg
	4,4'-azobis(4-cyanopentanoic acid)	0.140 g
20	Feed:	
	HEMA	31.7 g
	iPrCo(III)DMG	4.4 mg

The water was degassed under nitrogen in a multi-necked 250 mL reactor equipped with a mechanical stirrer and heated to 80°C. The initial shot was then added and the monomer feed was added over 90 min by syringe pump. On completion of the feed further initiator (0.070 g) was added and the temperature was held at 80°C for 180 min. The conversion based on % solids was > 90%. NMR:  $\bar{M}_n$  1550

30 B. Preparation of Hydroxyethyl Methacrylate-*block*-Methyl Methacrylate

	HEMA compound (2) solution (30% in water) <sup>o</sup>	30 g
	isopropanol	40 g
	azobisisobutyronitrile	0.19 g
35	Monomer Feed:	
	HEMA	15.5 g

<sup>o</sup>from Part A



The HEMA compound (2) and isopropanol were placed in a multi-neck 250 mL reactor fitted with a mechanical stirrer, degassed under vacuum, then heated to 80°C under nitrogen. The initiator was added and the monomer feed commenced and added over 120 min by syringe pump. Further aliquots of initiator were added at 90 min (0.09 g) and 180 min (0.07 g). The reaction was held at 80°C for a further 90 min. The conversion based on % solids was > 90%.  
 GPC:  $\bar{M}_n$  3620,  $\bar{M}_w$  6650; Dispersity 1.83

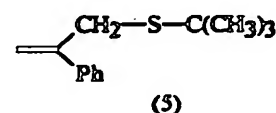
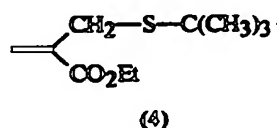
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EXAMPLES 50-52

This procedure illustrates the preparation of blocks from compounds (2) prepared with addition-fragmentation transfer agents in emulsion polymerization. Use of these reagents allows a wide range of end-group functionality to be introduced into the final product.

The recipe is compatible with a one-pot synthesis of block-copolymer from transfer agent and monomers.

Preparation of Methyl Methacrylate-*block*-Butyl Methacrylate



A. Preparation of MMA compound (2)			
20	Water		37.5 g
	SDS (3 % aq. solution)		3 g
25	Shot:	MMA	1.56 g
		allyl sulfide 4	0.078 g
		4,4'-azobis(4-cyanopentanoic acid)	0.071 g
	Feed 1: (0.188 mL/min)	MMA	14.04 g
		allyl sulfide 4	0.668 g
30	Feed 2: (0.188 mL/min)	MMA	5 g

The water, SDS were combined and degassed under vacuum in a multi-necked 250 mL reactor equipped with a mechanical stirrer. The mixture was heated to 80°C under nitrogen and the shot added. Feed 1 was added over 80 min by syringe pump. Feed 2 was then added over 28 min. On completion of the feeds the temperature was held at 80°C for a further 90 min. The conversion based on % solids was 98%.  
 GPC:  $\bar{M}_n$  5520  $\bar{M}_w$  8770; Dispersity 1.59.

B. Preparation of MMA-block-BMA.

MMA compound (2) latex 27.1 g  
 (ca. 32 % solids)<sup>a</sup>  
 SDS (3 % aq. solution) 1.0 g  
 Initiator Feed: (0.316 mL/min)  $K_2S_2O_8$  (0.36 wt % aq. solution) 23.7 g  
 Monomer Feed: (0.218 mL/min) nBMA 15.5 g

<sup>a</sup>from Part A

The MMA compound (2) latex and SDS was placed in a multi-neck 250 mL reactor, degassed under vacuum, then heated to 80°C under nitrogen. The initiator and monomer feeds were added concurrently over 70 min. After monomer addition was complete the reaction was held at 80°C for 90 min. The conversion based on % solids was 98%.

GPC:  $\bar{M}_n$  12600,  $\bar{M}_w$  17200; Dispersity 1.36

25

Table 7. Block Copolymers by Emulsion Polymerization

Example	Monomer	Transfer Agent <sup>a</sup>	Compound (2)			Block	
			Composition	$\bar{M}_n^b$	Disp.	$\bar{M}_n^b$	Disp.
50	nBMA	4	MMA	5520	1.59	12600	1.36
51	MMA	4	nBMA	5300	1.57	7300	1.43
52	nBMA	5 <sup>c</sup>	MMA	5450	1.57	24700	1.46

<sup>a</sup>Compound (2) prepared with addition-fragmentation transfer agent indicated.

<sup>b</sup>GPC (polystyrene equivalents).

<sup>c</sup>Compound (2) synthesis carried out at 90°C

EXAMPLES 53 - 56

This procedure illustrates the preparation of blocks from compounds (2) prepared with addition-fragmentation transfer agents by solution polymerization. Use

of these reagents allows a wide range of monomers to be used and permits various end-group functionality to be introduced into the final product.

#### Preparation of Styrene-*block*-p-methylstyrene

##### A. Preparation of Styrene compound (2)

5		Styrene	30.10 g
		Butyl acetate	10.03 g
		allyl sulfide <sup>o</sup>	1.63 g
	Feed 1: (0.210 mL/min)	Styrene	39.98 g
10		allyl sulfide <sup>o</sup>	6.67 g
	Feed 2: (0.063 mL/min)	1,1'-azobis(4-cyclohexanecarbonitrile)	0.283 g
		Butyl acetate	20.01 g

15 The styrene solution was degassed under nitrogen in a multi-necked 250 mL reactor equipped with a mechanical stirrer. The mixture was heated to reflux (125°C) under nitrogen and the feeds added over 240 min by syringe pump. The compound (2) was isolated by two precipitations into acidified methanol. The conversion based on isolated compound (2) was 50%.

20 GPC:  $\bar{M}_n$  1880  $\bar{M}_w$  2950; Dispersity 1.57.

##### B. Preparation of Styrene-*block*-p-Methylstyrene.

		Styrene compound (2) <sup>o</sup>	4.02 g
		Butyl acetate	3.53 g
		p-Methylstyrene	0.46 g
25			
	Initiator Feed: (0.0177 mL/min)	1,1'-azobis(4-cyclohexanecarbonitrile)	0.108 g
		Butyl acetate	25.13 g
	Monomer Feed: (0.0132 mL/min)	p-Methylstyrene	19.01 g

30 <sup>o</sup> from Part A

35 The styrene compound (2) and butyl acetate were placed in a multi-neck 100 mL reactor under nitrogen and heated to reflux (ca. 125°C). After 10 min, the p-methylstyrene was added. The initiator and monomer feeds were then commenced and added over 24 h. The conversion based on monomer consumption was 84%.  
GPC:  $\bar{M}_n$  9500,  $\bar{M}_w$  24620; Dispersity 2.59 (includes compound (2) peak)

Table 8. Styrene Block Copolymers by Solution Polymerization

Example	Monomer	Transfer Agent <sup>a</sup>	Compound (2)		Block			
			M <sub>n</sub> <sup>b</sup>	Disp.	M <sub>n</sub> <sup>b</sup>	Disp.	Solvent	% Conv. <sup>c</sup>
53	pMS	4	1830	1.59	17260	1.61	BAC	90
54	nBMA	4	1830	1.59	9120	1.43	MEK	80
55	nBMA	4	1830	1.59	17930	1.62	BAC	60
56	nBMA	5	2330	1.55	16870	1.42	MEK	50

<sup>a</sup>Compound (2) prepared with addition-fragmentation transfer agent indicated.

<sup>b</sup>GPC (polystyrene equivalents).

<sup>c</sup>approx conversion of compound (2) to block. Monomer conversion is >85%.

5

### EXAMPLES 57 - 64

These examples describe a generalized process for the preparation of narrow polydispersity block copolymers and homopolymers by solution polymerization using vinyl compounds (2) selected from methacrylate dimers and trimers.

The general procedure for the polymerization is to slowly add the selected monomer(s), (i), and free radical initiator (iii) to the unsaturated transfer agent (2) at a rate to avoid excessive buildup in monomer concentration. A small amount of monomer(s) can be added to the transfer agent before the start of polymerization.

The polymerization reaction is started by heating the reactor containing (2) to the desired temperature and starting the gradual and continuous feeds of monomer(s) and free radical initiator.

The length of the polymerization time is dependant upon the temperature chosen and the molecular weight of the polymer desired. Higher temperatures allow for faster monomer feed rates and shortened times.

The choice for initiator depends upon the temperature used. It is convenient to add the initiator either in a solvent or mixed with some of the monomer(s) by means of a controlled rate feeder pump. When no solvent is used, the polymerization runs under bulk conditions at a well controlled rate.

In this process, the amount of initiator does not limit the polymer molecular weight. Reaction of unsaturated ends of (2) controls the degree of polymerization. The total number of moles of free radical initiator is generally set to be less than 15-20% of the number of moles of (2) used in the process.

The following Tables illustrate some of the specific polymers and

their conditions for polymerization which have been practiced using this procedure.

Table 9: Solution Process Conditions

Ex.	Vinyl Transfer Agent	Monomer(s)	Temp. °C	Initiator	Polymeriz. Time hr	Comments
57	MMA <sub>3</sub>	MMA	60	VAZO 52 4.29 gm	29.8	25 gm MMA at start
	100 gm	500 gm		300 ml EAc		
58	MMA <sub>3</sub>	30:70 GMA/CHMA	60	VAZO 52 13.1 gm	30	36 gm monomer mix at start
	90 gm	1400 gm		386 ml EAc		
59	MMA <sub>3</sub>	GMA	60	VAZO 52 10.4 gm	29.4	16 gm GMA at start
	50 gm	322 gm		290 ml EAc		
		50:50 MMA/BMA				add GMA then MMA/BMA mix
		710 gm				
60	MMA <sub>3</sub>	30:70 GMA/MMA	100-132	VAZO 88 12.5 gm	9.7	50 gm monomer mix at start
	200 gm	1115 gm		228 ml BAc		
61	GMA <sub>2</sub>	15.6:84.4 GMA/MMA	120	VAZO 88 21.7 gm	16.6	15 gm monomer mix at start
		1460 gm		346 ml BAc		
62	GMA <sub>2</sub>	12:26:62 IBMA/GMA/MMA	130	VAZO 88 11.6 gm	11.5	5 gm monomer mix at start
		537 gm		204 ml BAc		
63	GMA <sub>2</sub>	23:20:57 BMA/GMA/MMA	120	VAZO 88 12.8 gm	24	2 gm monomer mix at start
		755 gm		203 ml BAc		
64	GMA <sub>2</sub>	10:32:58 IBMA/GMA/MMA	140	t-butyl-perbenzoate	9.9	13 gm monomer mix at start
		455 gm		6.8 gm		

5

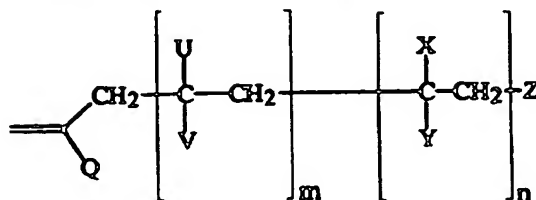
Table 10 summarizes the polymerization illustrated in Table 9.

Table 10: Summary of Narrow Polydispersity Polymers Made by Solution Process

Example	Polymer Description	Mn (by GPC)	Dispersity
57	MMA <sub>n</sub>	2700	1.38
58	MMA <sub>2</sub> //GMA <sub>m</sub> CHMA <sub>n</sub> MMA <sub>p</sub> //MMA	4970	1.44
59	MMA <sub>2</sub> //GMA <sub>m</sub> //MMA <sub>n</sub> BMA <sub>p</sub> //MMA	6800	1.48
60	MMA <sub>2</sub> //GMA <sub>m</sub> MMA <sub>n</sub> //MMA	2170	1.44
61	GMA//MMA <sub>m</sub> GMA <sub>n</sub> //GMA	3360	1.43
62	GMA//MMA <sub>m</sub> IBMA <sub>n</sub> GMA <sub>p</sub> //GMA	3420	1.3
63	GMA//MMA <sub>m</sub> BMA <sub>n</sub> GMA <sub>p</sub> //GMA	4560	1.49
64	GMA//MMA <sub>m</sub> BMA <sub>n</sub> GMA <sub>p</sub> //GMA	2880	1.43

CLAIMS

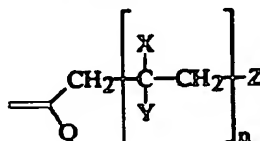
1. A process for the synthesis of polymers of the general formula:



1

comprising contacting:

- 5 (i) a vinyl monomer of the formula  
 $\text{CH}_2 = \text{CUV}$   
 (ii) a vinyl-terminated compound of formula



2

and

- (iii) free radicals, produced from a free radical source; and  
 10 increasing the molar amount of polymers by one or both of:  
 (a) decreasing the molar amount of (iii) for any given conversion of (i);  
 and  
 (b) decreasing the molar amount of (i) for any given conversion of (iii);

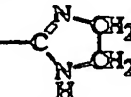

wherein:

- 15 Q is selected from the group H, R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;  
 U is selected from H and R;  
 V is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;  
 20 X is selected from H and R;  
 Y is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;  
 Z is selected from the group H, SR<sup>1</sup>, S(O)R, S(O)<sub>2</sub>R, R<sup>2</sup> and R<sup>3</sup>;  
 R is selected from the group substituted and unsubstituted alkyl, aryl, aralkyl,  
 25 alkaryl and organosilyl groups wherein the substituent(s) are independently

selected from the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

$R^1$  is selected from the group H, substituted and unsubstituted alkyl, aryl, aralkyl, alkaryl, organosilyl wherein the substituent(s) are independently selected from the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

$R^2$  is selected from the group free radical initiator-derived fragments of substituted and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl, alkoxyaryl, sulfate groups wherein the substituent(s) are independently selected from R,  $OR^1$ ,  $O_2CR$ , halogen,  $CO_2H$  (and salts),  $CO_2R$ , CN,  $CONH_2$ .

$CONHR$ ,  $CONR_2$ ,  (and salts) and  (and salts);

$R^3$  is selected from the group radical chain transfer agent-derived fragments of substituted and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl, alkoxyaryl, and  $PR_2$  groups wherein the substituent(s) are independently selected from R,  $OR^1$ , SR,  $NR_2$ , NHR,  $O_2CR$ , halogen,  $CO_2H$ ,  $CO_2R$ , CN,  $CONH_2$ ,  $CONHR$ , and  $CONR_2$ ;

m and n are independently  $\geq 1$ ; and

when either or both of m and n are greater than 1, the repeat units are the same or different.

2. A process according to Claim 1 wherein (i) is selected from one or more of following monomers, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha methyl styrene, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylate, acrylates and styrene selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-tert-butyl methacrylamide, N-n-butyl methacrylamide, N-methyl-ol methacrylamide, N-ethyl-ol methacrylamide, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methyl-ol acrylamide, N-ethyl-ol acrylamide, vinyl benzoic

acid, diethylamino styrene, alpha-methylvinyl benzoic acid, diethylamino  
 alpha-methylstyrene, para-methylstyrene, p-vinyl benzene sulfonic acid,  
 trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate,  
 tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate,  
 5 diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate,  
 diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate,  
 diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate,  
 diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate,  
 triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate,  
 10 dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate,  
 dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate,  
 dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl  
 acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, and vinyl butyrate, vinyl  
 chloride, vinyl fluoride, vinyl bromide.

15

3. A process according to Claim 1 wherein (ii) is selected where Q, -XYC-  
 CH<sub>2</sub>-, Z and "n" are independently selected from one or more of the following:

Q = H, methyl, ethyl, butyl, cyclohexyl, methoxy, ethoxy, propoxy, butoxy,  
 phenoxy, acetate, propionate, butyrate, benzoate, carboxylate, chlorine,  
 20 bromine, fluorine, iodine, nitrile, amide, N-methylamide, N-ethylamide, N-  
 propylamide, N,N-dimethylamide, N,N-diethylamide, N,N-dibutylamide, N-  
 methyl-N-ethylamide, carboxylate ester of methyl, ethyl, propyl, butyl,  
 benzyl, phenyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 4-  
 hydroxy-butyl, 3-hydroxybutyl, 2-hydroxybutyl, 3-trimethoxysilylpropyl, 3-  
 25 triethoxysilylpropyl, 3-tributoxy-silylpropyl, 3-tri(isopropoxy)silylpropyl, 2-  
 aminoethyl, 3-amino-propyl, 2-aminopropyl, 4-aminobutyl, 3-aminobutyl,  
 2-aminobutyl, 2-epoxypropyl, or 3-epoxypropyl;

-XYC-CH<sub>2</sub>- = derived from one or more of the following monomers: methyl  
 methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate,  
 30 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl  
 methacrylate, phenyl methacrylate, methacrylonitrile, styrene, alpha methyl  
 styrene, glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl  
 methacrylate, hydroxybutyl methacrylate, diethylaminoethyl methacrylate,  
 triethyleneglycol methacrylate, N-tert-butyl methacrylamide, N-n-butyl  
 35 methacrylamide, N-methyl-ol methacrylamide, N-ethyl-ol methacrylamide,  
 trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate,  
 tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate,  
 diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl



- methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, diethylaminoethyl acrylate, triethyleneglycol acrylate, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methyl-ol acrylamide, N-ethyl-ol acrylamide, vinyl benzoic acid, diethylamino styrene, p-vinyl benzene sulfonic acid, para-methylstyrene, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, and vinyl butyrate.
- 5      Z = H, SR<sup>1</sup>, S(O)R, S(O)<sub>2</sub>R, R<sup>2</sup>, or R<sup>3</sup>;
- 10      R = methyl, ethyl, propyl, n-butyl, tert-butyl, isobutyl, phenyl, benzyl, 2-phenylpropyl, trimethoxysilylpropyl, tributoxysilyl-propyl, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 2-epoxypropyl, 2-aminoethyl, 2-amino-propyl, methoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxy-propyl, or heptafluoropropyl;
- 15      R<sup>1</sup> = hydrogen, methyl, ethyl, propyl, n-butyl, tert-butyl, isobutyl, phenyl, benzyl, 2-phenylpropyl, trimethoxysilyl-propyl, tributoxysilylpropyl, hydroxymethyl, 2-hydroxyethyl, 2-hydroxypropyl, 2-epoxypropyl, 2-aminoethyl, 2-aminopropyl, methoxymethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxypropyl, or heptafluoropropyl;
- 20      R<sup>2</sup> = 2,4-dimethylpentanenitrile, 2-methylbutanenitrile, 2-methylpropanenitrile, cyclohexanecarbonitrile, 4-cyanopentanoic acid, N,N'-dimethyleneisobutyramidine, N,N'-dimethyleneisobutyramidine hydrochloride, 2-amidinopropane, 2-amidinopropane hydrochloride, 2-methyl-N-[1,1-bis(hydroxymethyl)ethyl] propionamide, 2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2-methyl-N-(2-hydroxyethyl) propionamide, isobutyramide hydrate, hydroxyl, or sulfate;
- 25      R<sup>3</sup> = 1,1-bis(carboethoxy)ethyl, 1,1-bis(carbomethoxy)ethyl, bis(carboethoxy)-methyl, bis(carbomethoxy)methyl, 1-carboethoxy-1-phenyl ethyl, 1-carbomethoxy-1-phenyl ethyl, chlorine, bromine, fluorine, iodine, 1-methyl-1-[carbo(2-epoxypropoxy)]ethyl, 1-methyl-1-[carbo(2-hydroxyethoxy)]ethyl,
- 30      1-methyl-1-[carbo(2-epoxypropoxy)]ethyl, 1-methyl-1-[carbo(2-hydroxyethoxy)]ethyl,
- 35      1-methyl-1-[carbo(2-epoxypropoxy)]ethyl, 1-methyl-1-[carbo(2-hydroxyethoxy)]ethyl,

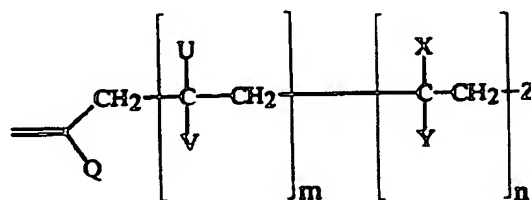
- 1-methyl-1-[carbo(4-hydroxy-butoxy)]ethyl, 1-methyl-1-[carbo(2-aminoethoxy)]ethyl, 1-methyl-1-[carbo(3-trimethoxysilylpropoxy)]ethyl, 1-methyl-1-[carbo(3-triethoxysilylpropoxy)]ethyl, 1-methyl-1-[carbo(3-dimethoxyethoxysilylpropoxy)]ethyl, 1-methyl-1-[carbo(2-methoxyethoxy)]ethyl, (N,N-di-methylamino)(cyano)methyl, N,N-dimethylamino-(benzo)methyl, thiomethyl(cyano)methyl, or thioethyl(cyano)methyl;  
 5  $n \geq 1$  and when greater than 1, the repeat units are the same or different.

4. A process according to Claim 1 wherein (iii) is selected from one or more  
 10 of the following: 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-cyanpentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl] propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]-propionamide, 2,2'-azobis(N,N'-dimethylene-isobutyramidine) dichloride, 2,2'-azobis(2-amidinopropane) dichloride, 2,2'-azobis(N,N'-dimethyleneisobutyramide), 2,2'-  
 15 azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl] propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl] propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propionamide], 2,2'-azobis(iso-butylamide) dihydrate, t-butylperoxyacetate, t-butylperoxybenzoate, t-butylperoxyoctoate, t-butylperoxyneodecanoate, t-butylperoxyiso-butylate, t-amylperoxypivalate, t-butylperoxypivalate, cumene hydroperoxide, dicumyl peroxide, benzoyl peroxide, potassium persulfate, ammonium persulfate.

5. Process of Claim 1 wherein compound (2) is a block copolymer of  
 25 general structure (1) and the product is a tri- or multi-block copolymer.

6. Process of Claim 1 employing a temperature above 100°C.

7. A composition consisting essentially of a polymer with a polydispersity  
 30 <1.7, having the formula



1

wherein:

Q is selected from the group H, R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;

U is selected from H and R;

5 V is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;

X is selected from H and R;

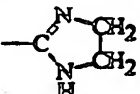

Y is selected from R, OR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR and CONR<sub>2</sub>;

Z is selected from the group H, SR<sup>1</sup>, S(O)R, S(O)<sub>2</sub>R, R<sup>2</sup> and R<sup>3</sup>;

10 R is selected from the group substituted and unsubstituted alkyl, aryl, aralkyl, alkaryl and organosilyl groups wherein the substituent(s) are independently selected from the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

15 R<sup>1</sup> is selected from the group H, substituted and unsubstituted alkyl, aryl, aralkyl, alkaryl, organosilyl wherein the substituent(s) are independently selected from the group carboxyl, epoxy, hydroxyl, alkoxy, amino and halogen;

20 R<sup>2</sup> is selected from the group free radical initiator-derived fragments of substituted and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl, alkoxyaryl, sulfate groups wherein the substituent(s) are independently selected from R, OR<sup>1</sup>, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H (and salts), CO<sub>2</sub>R, CN, CONH<sub>2</sub>,

CONHR, CONR<sub>2</sub>,  (and salts) and  (and salts);

25 R<sup>3</sup> is selected from the group radical chain transfer agent-derived fragments of substituted and unsubstituted alkyl, cycloalkyl, aryl, aralkyl, alkaryl, organosilyl, alkoxyalkyl, alkoxyaryl, and PR<sub>2</sub> groups wherein the substituent(s) are independently selected from R, OR<sup>1</sup>, SR, NR<sub>2</sub>, NHR, O<sub>2</sub>CR, halogen, CO<sub>2</sub>H, CO<sub>2</sub>R, CN, CONH<sub>2</sub>, CONHR, and CONR<sub>2</sub>;

m and n are independently ≥ 1; and

30 when either or both of m and n are greater than 1, the repeat units are the same or different.

8. A composition according to Claim 7 wherein the polydispersity is < 1.5.

35 9. A polymer made by the process of Claim 1.

10. A polymer made by the process of Claim 5.

# INTERNATIONAL SEARCH REPORT

International Application No.  
**PCT/US 95/14428**

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC 6 C08F2/38**

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC 6 C08F**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 12568 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 11 May 1995 see the whole document ---	1-10
A	EP,A,0 261 942 (DU PONT DE NEMOURS AND COMPANY) 30 March 1988 see claims 1-14 ---	1
A	EP,A,0 597 747 (RHONE-POULENC CHIMIE) 18 May 1994 see claims 1-7 ---	1
A	WO,A,92 09639 (BAUSCH & LOMB INCORPORATED) 11 June 1992 see claims 1-16 ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*d\* document member of the same patent family

Date of the actual completion of the international search

**18 March 1996**

Date of mailing of the international search report

**- 4. 04. 96**

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# INTERNATIONAL SEARCH REPORT

Intern al Application No  
PCT/US 95/14428

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO,A,93 22355 (DU PONT DE NEMOURS AND COMPANY) 11 November 1993 cited in the application see claims 1-68 -----</p>	1

1

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Information on patent family members

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